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(54) **Flame retardant resin composition and flame retardant insulated cable.**

(57) A flame retardant resin composition is described, comprising a resin material containing as a main component a graft copolymer prepared by graft copolymerizing an ethylene/lower alkyl methacrylate copolymer with vinyl chloride; and at least one member selected from the group consisting of an organic flame retarder, an inorganic flame retarder, and an inorganic filler. A flame retardant insulated cable is also described, comprising a conductor coated with an insulator of polyethylene having a high softening point. The insulator is then coated with the flame retardant resin compsition of the present invention.

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FLAME RETARDANT RESIN COMPOSITION AND FLAME RETARDANT INSULATED CABLE

FIELD OF THE INVENTION

The present invention relates to a flame retardant resin composition, and particularly to sheath materials to flame-retard a high voltage cable, for example, that used for high voltage circuits in electron guns of the cathode ray tube of television receivers. The present invention also relates to a flame retardant insulated cable using the flame retardant resin composition.

BACKGROUND OF THE INVENTION

Various attempts have been made to manufacture a high voltage cable, for example, that used for high voltage circuits in electron guns of cathode ray tubes of television receivers, including a method in which an insulator mainly made of polyethylene is applied on a wire, followed by applying on the insulator a flame retardant material to protect the inner polyethylene. Such a method is, for example, disclosed in JP-B-51-8465 (The term "JP-B" as used herein means an "examined Japanese patent publication").

According to JP-B-51-8465, a polyethylene having a high softening point of 105°C or more is used as an insulator, the softening point corresponding to the temperature of 105°C stipulated in Subject 758 of United States UL standard. The polyethylene of the publication is applied on a wire, followed by applying on the polyethylene a flame retardant sheath material comprising as a main component a graft copolymer prepared by graft copolymerizing an ethylene/vinyl acetate copolymer with vinyl chloride, thereby obtaining a wire having tracking resistance, high tension cut-through characteristics, and high resistance to deformation, together with the use of the polyethylene insulator of the high softening point.

JP-B-52-41786 shows further improvement in such flame retardant sheath materials. In this publication, (1) an inorganic flame retarder comprising at least one of oxides or sulfides of antimony, arsenic or tin; (2) an organic flame retarder comprising a halogen-containing compound having molecular weight of 200 to 1,500; and (3) an inorganic filler for sintering are further added to the above graft copolymer, thereby improving flameproofness relative to the flame retardant sheath materials containing only the above graft copolymer.

There have been known a number of techniques to provide such flame retardant sheath materials.

For example: (1) JP-B-53-47148 shows that a graft copolymer of a chlorinated polyethylene and vinyl chloride are crosslinked by means of radicals or high energy radiation. (2) JP-B-54-14611 shows that a chlorinated polyethylene is mixed with a graft copolymer prepared by grafting vinyl chloride on to an ethylene/vinyl ester copolymer. (3) JP-B-54-14612 shows that antimony trioxide is mixed with the above mixture of the JP-B-54-14611. (4) JP-B-54-15057 shows that a chlorinated polyethylene is added to a graft copolymer of a chlorinated polyethylene and vinyl chloride. (5) JP-B-54-15058 shows that an ethylene copolymer is added to a graft copolymer of a chlorinated polyethylene and vinyl chloride. (6) JP-B-56-41654 shows that a metal borate and calcium carbonate are mixed with a graft copolymer prepared by grafting vinyl chloride on to an ethylene vinyl ester copolymer. (7) JP-B-56-41655 shows that a hydrated alumina is added to the above mixture of the JP-B-56-41654. (8) JP-B-61-34746 shows that a chlorinated polyethylene is mixed with a zinc compound, and oxides or sulfides of antimony, zircon or molybdenum.

However, as mentioned in these publications, with conventional flame retardant sheath materials, a flame retardant property precedes the other properties, and electrical properties, are compensated for by selecting insulating materials such as polyethylenes. In these inventions, no special regard is paid to electrical properties, as affected by sheath materials.

On the other hand, as electronic equipment has increased in size and function, the electrical properties of sheath materials, particularly under high temperature, have not been negligible. As a practical matter, it is very important that sheath materials maintain their insulating performance in an atmosphere of 60°C or more.

SUMMARY OF THE INVENTION

An object of the present invention is to overcome the above-noted problems inherent in the prior art so as to provide a flame retardant resin composition that, in addition to a high flame retardant property, provides improved electrical properties at room temperature or more, and can be used to produce a flame retardant insulated wire.

Other objects and effects of the present invention will be apparent from the following description.

The present invention is characterized by the use of a graft copolymer prepared by graft copolymerizing an ethylene/lower alkyl methacrylate copolymer with vinyl chloride.

The present invention relates to a flame retardant resin composition comprising a resin material containing as a main component a graft copolymer prepared by graft copolymerizing an ethylene/lower alkyl methacrylate copolymer with vinyl chloride; and at least one additional component selected from the group consisting of an organic flame retarder, an inorganic flame retarder, and an inorganic filler.

The present invention also relates to a flame retardant insulated cable comprising a conductor; an insulator comprising a polyethylene having a high softening point covering the conductor; and the flame retardant resin composition of the present invention applied on the insulator.

DETAILED DESCRIPTION OF THE INVENTION

The proportion of each of the components which constitute the graft copolymer (which is hereinafter referred to as the "graftmer") can be optionally selected depending on the usage. Generally, the ethylene content of the backbone copolymer is 40 to 95 wt%, preferably 50 to 90 wt%, and the lower alkyl methacrylate content of the backbone polymer is 5 to 60 wt%, preferably 10 to 50 wt%. The content of the vinyl chloride to be graft copolymerized is 20 to 80 wt%, preferably 30 to 60 wt%.

Typical examples of the lower alkyl methacrylate constituting the backbone copolymer include methyl methacrylate, ethyl methacrylate, and propyl methacrylate. Of these methacrylates, methyl methacrylate is preferred.

The graftmer may be used alone, or in combination with other resins that are compatible with it.

In the present invention, when a compatible resin such as a polyethylene, a polypropylene, a polyvinyl alcohol, a vinyl chloride resin, or a chlorinated polyethylene is mixed with the graftmer, mechanical strength as well as flexibility can be controlled, and flame retardant properties as well as foaming expansion increase.

It is preferred that the graftmer is high in polymerization degree, for example, 1,000 to 5,000, more preferably from 1,000 to 2,000, from the standpoint of mechanical strength.

The graftmer used in the present invention can be prepared by known methods as described, e.g., in JP-A-61-155414 (The term "JP-A" as used herein means an "unexamined published Japanese patent application").

When the graftmer is singly used, or it is only mixed with a compatible resin (i.e., the organic or inorganic flame reterder or the inorganic filler is not used), flame retardant properties are insufficient, and it is difficult to keep foaming expansion. Accordingly, it is liable to cause flame spread and catch fire.

These deficiencies are overcome in the present invention, by adding at least one member selected from the group consisting of an organic flame retarder, an inorganic flame retarder, and an inorganic filler to the graftmer.

Examples of the organic flame reterder include a halogen-containing organic compound and a phosphorus-containing organic compound. Typical examples of the halogen-containing organic compound include tetrabromobutane, perchloropentacyclodecane, tetrabromobisphenol A, chlorinated paraffin, bromotriphenylphosphate, decabromobiphenyl, decabromodiphenyl oxide, and bromoepoxide. Particularly preferred is an aromatic halogen compound, such as decabromobiphenyl and decabromodiphenyl oxide, from the standpoint of high temperature resistance.

Typical examples of an inorganic flame retarder include oxides or sulfides of antimony, arsenic, or tin. Particularly preferred is antimony trioxide.

In order to maintain flame retardant properties, it is desirable to mix the graftmer with an inorganic filler. Typical examples of such an inorganic filler include asbestos, talc, clay, mica, zinc borate, aluminum hydroxide, calcium carbonate, barium sulfate, magnesium oxide. Particularly preferred are talc, clay, and zinc borate.

In the present invention, an organic flame retarder, an inorganic flame retarder, and an inorganic filler can be added, singly or in combination in a suitable amount, to the graftmer so that the electric properties of the graftmer at room temperature or more, particularly, at 60 °C are improved in addition to high flame

retardant properties.

The amounts of the above components, i.e., the organic flame retarder, the inorganic flame retarder and the inorganic filler, may be widely varied according to the aim and use. Although the amounts of the above components can easily be determined by one skilled in the art according to the aim and use, the amount of the organic flame retarder is preferably from 10 to 50 parts by weight, more preferably from 15 to 40 parts by weight, based on 100 parts by weight of the graftmer; the amount of the inorganic flame retarder is preferably from 1 to 30 parts by weight, more preferably from 5 to 25 parts by weight, based on 100 parts by weight of the graftmer; and the amount of the inorganic filler is preferably from 5 to 50 parts by weight, more preferably from 5 to 25 parts by weight, based on 100 parts by weight of the graftmer.

Various additives may also be added to the compositon of the present invention, if desired. Specifically, examples of such additives include thermal stabilizers, crosslinking agents (including a peroxide), other fillers, foaming agents, lubricants, dyes and pigments.

It is preferred that a hindered amine light stabilizer (which is hereinafter referred to as "HALS") is further mixed with the flame retardant resin composition of the present invention.

The amount of HALS is preferably from 0.5 to 5 parts by weight, and more preferably from 1 to 3 parts by weight, based on 100 parts by weight of the graftmer. if the amount of HALS is less than 0.5 parts by weight, it has little effect on electric properties. The amount of HALS may be above 5 parts by weight, for example, 10 to 20 parts by weight. In this case, the thermal aging resistance much increases, thereby decreasing the amount of a inhibitor of aging. However, the upper limit of 5 parts by weight is preferred from the standpoint of cost.

The flame retardant resin composition of the present invention can be manufactured using a single screw extruder, a multiple screw extruder, Banbury mixer, a roller mill, a kneading machine, a high speed fluid agitator of Henschel mixer type, or any apparatus, that will cause each component to be mixed at a temperature over the melting point of thermoplastic resins.

The composition of the present invention is advantageously used in a cover for an electric cable (particularly as a sheath material). Further, it is applicable to products which require flame retardant properties, such as injection molded articles, tubes, extruded articles, compression molded articles, calendered articles, stretched articles, and foamed articles.

The flame retardant insulated cable of the present invention may be manufactured as follows:

A conductor, such as copper, is covered with an insulator, such as a polyethylene having a high softening point, to a suitable thickness. The insulator is preferably a flame-retarded insulator, for example, those mixed with a chlorinated polyethylene or a flame retarder. The insulator, if necessary, may be crosslinked. Subsequently, a flame retardant resin composition containing the graftmer of the present invention is applied on the insulator. The composition of the present invention may be crosslinked by means of ionizing radiation if desired.

Examples of polyethylene having a high softening point for use as the insulator include a moderate-pressure polyethylene, a low-pressure polyethylene, or a high-density polyethylene, each having a softening point of 105°C or more. It is preferred that these polyethylenes be crosslinked by means of high energy radiation.

The application of a polyethylene having a high softening point as an insulator on a conductor together with the composition of the present invention as a sheath material provides a flame retardant insulated cable that is extremely improved in electrical properties at room temperature or more.

A typical example of conventional flame retardant resin compositions acting as sheath materials is disclosed in JP-B-52-41786 in which a graftmer prepared by graft copolymerizing an ethylene/vinyl acetate copolymer with vinyl chloride is mixed with flame retarders and inorganic fillers. An electrical property of this conventional composition, which is typical as common insulating materials, is that the volume resistance decreases with an increase in temperature, and becomes lower than 10^{11} Ωcm, which corresponds to the critical value of an insulator in an atmosphere of high temperature.

The reason why the use of the graftmer of the present invention maintains insulating properties even in an atmosphere of high temperature is not yet theoretically understood.

However, this result is particularly surprising and thereby provides a high flame retardant sheath material capable of maintaining insulating properties even in an atmosphere of high temperature.

As discussed above, the graftmer per se used in the present invention is not high in flame retardant properties. Therefore, it is necessary to mix the graftmer with flame retarders and/or inorganic fillers, as taught by the present invention.

The present invention is described in greater detail with reference to the following examples, although it is not limited thereto.

EXAMPLE 1

Flame retardant resin compositions A, B and C according to the present invention having components and weight ratios shown in Table 1 were prepared by the use of a 6 inch open roll mill and then pressed at 150°C to produce 1 mm-thick sheets. These sheets were irradiated by electron rays at 10 Mrad to crosslink the polymer.

The volume resistivities of the sheets as a function of temperature was determined. Table 2 shows the results. It can be seen from the data in Table 2 that a volume resistivity of 10^{11} Ωcm, which means good insulating properties, is maintained even at a temperature as high as 80°C.

Comparative compositions X and Y were produced in the same manner as in the above procedures except that the kinds of components were varied as shown in Table 1. The change in the volume resistivities as a function of temperature of the comparative compositions was also determined. Table 2 also shows the results. As can be seen from the data in Table 2, the volume resistivities were less than 10^{11} Ωcm at 80°C, which mean poor insulating properties.

In Example 1, the graftmers used are as follows:

Graftmer 1: ethylene/methyl methacrylate copolymer (the content of vinyl chloride grafted is 50 wt%, the methyl methacrylate content is 38 wt% and the polymerization degree is 1,030).

Graftmer 2: ethylene/methyl methacrylate copolymer (the content of vinyl chloride grafted is 45 wt%, the methyl methacrylate content is 38 wt% and the polymerization degree is 1,480).

Graftmer 3: ethylene/methyl methacrylate copolymer (the content of vinyl chloride grafted is 40 wt%, the methyl methacrylate content is 38 wt% and the polymerization degree is 1,230).

Graftmer 4: graft copolymer prepared by graft copolymerizing an ethylene/vinyl acetate copolymer with vinyl chloride (Sumigraft GF manufactured by Sumitomo Chemical Co., Ltd.).

Table 1

	Composition				
Component	A	B	C	X	Y
Graftmer 1	100	-	-	-	-
Graftmer 2	-	100	-	-	-
Graftmer 3	-	-	100	-	-
Graftmer 4	-	-	-	100	100
Tribasic lead sulfate	10	10	-	10	-
Dibasic lead sulfate	-	-	10	-	10
Stearic acid	1	1	1	1	1
Antimony trioxide	10	10	10	10	10
Zinc borate	10	10	10	10	10
Decabromodiphenyloxide	20	20	20	20	20
Clay	-	-	20	20	-
Talc	20	20	-	-	20
Anti-oxidizing agent[1)]	1	1	1	1	1
Note:					

1) 4,4′-thiobis-(6-tert-butyl-3-methylphenol)

Table 2

Volume resistivity (Ωcm)					
Measurement temperature (°C)	Composition				
	A	B	C	X	Y
Room temperature	1.7×10^{13}	3.7×10^{13}	6.1×10^{13}	5.6×10^{12}	7.5×10^{12}
40	1.1×10^{13}	3.6×10^{12}	2.4×10^{13}	1.8×10^{12}	1.6×10^{12}
60	2.3×10^{12}	8.4×10^{11}	5.5×10^{12}	2.7×10^{11}	3.3×10^{11}
80	1.1×10^{11}	1.3×10^{11}	2.4×10^{11}	3.9×10^{10}	3.5×10^{10}

EXAMPLE 2

Flame retardant resin compositions D and E according to the present invention having components and weight ratios shown in Table 3 were mixed by the use of a 6 inch open roll mill and then pressed at 150°C to produce 1 mm-thick sheets. These sheets were irradiated by electron rays at 10 Mrad to crosslink the polymer.

The volume resistivities of the sheets as a function of temperature was determined. Table 4 shows the results. It can be seen from the data in Table 4 that a volume resistivity of 10^{11} Ωcm, which means good insulating properties, is maintained even at a temperature as high as 80°C.

Comparative composition Z was produced in the same manner as in the above procedures except that the kinds of components were varied as shown in Tabel 3. The change in the volume resistivity as a function of temperature of the comparative composition was also determined. Table 4 shows the results. As can be seen from the data in Table 4, the volume resistivity is less than 10^{11} Ωcm at 80°C, which mean poor insulating properties.

In Example 2, the graftmers 2 and 4 are the same as used in Example 1. Graftmer 5 is as follows:

Graftmer 5: ethylene/methyl methacrylate copolymer (the content of vinyl chloride grafted is 40 wt%, and the polymerization degree is 1,370).

Table 3

	Composition		
Component	D	E	Z
Graftmer 2	100	-	-
Graftmer 5	-	100	-
Graftmer 4	-	-	100
Dibasic lead phosphite	10	10	10
Stearic acid	1	1	1
Antimony tioxide	10	10	10
Zinc borate	10	10	10
Decabromodiphenyloxide	20	20	20
Talc	20	20	20
Anti-oxidizing agent[1)]	1	1	1
HALS[2)]	2	2	-
Note:			

1) 4,4'-thiobis-(6-tert-butyl-3-methylphenol)
2) poly((6-(1,1,3,3-tetramethylbutyl)imimo-1,3,5-triazine-2,4-dyl)((2,2,6,6-tetramethyl-4-piperidyl)imino)-hexamethylene((2,2,6,6-tetramethyl-4-piperidyl)imino))

Table 4

Volume resistance (Ωcm)			
Measurement temperature (°C)	Composition		
	D	E	Z
Room temperature	4.9×10^{14}	6.2×10^{14}	7.5×10^{12}
40	1.3×10^{14}	4.2×10^{14}	1.6×10^{12}
60	7.9×10^{12}	2.6×10^{13}	3.3×10^{11}
80	3.5×10^{11}	6.9×10^{11}	3.5×10^{10}

It can be understood from the results shown in Tables 2 and 4 that the flame retardant resin composition of the present invention has, in addition to a high flame retardant property, excellent electrical properties at room temperature or higher. When HALS is further added to the resin composition of the present invention, the electrical properties are further improved.

As mentioned above, since the flame retardant resin composition of the present invention maintains insulating properties even in an atmosphere of high temperature, it can be used for sheath materials that are applied to a high voltage wire, a shielding wire, or a coaxial cable; these wires being used, for example, in the high voltage circuits of an electron gun in television cathode ray tube, thereby maintaining excellent electrical properties.

Further, the combination of a polyethylene of high softening point acting as an insulator and the above sheath materials provides a flame retardant insulated cable having excellent electric properties at room temperature or more.

While the invention has been described in detail and with reference to specific embodiment thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A flame retardant resin composition comprising a resin material containing as a main component

(A) a graft copolymer prepared by graft copolymerizing an ethylene/lower alkyl methacrylate copolymer with vinyl chloride; and

(B) at least one member selected from the group consisting of

(i) an organic flame retarder,

(ii) an inorganic flame retarder, and

(iii) an inorganic filler.

2. A flame retardant resin composition as claimed in claim 1, wherein said resin material further comprising (C) a hindered amine light stabilizer.

3. A flame retardant resin composition as claimed in claim 1, wherein the resin content of said ethylene/lower alkyl methacrylate copolymer is from 40 to 95 wt%; and the lower alkyl methacrylate content of said ethylene/lower alkyl methacrylate copolymer is from 5 to 60 wt%.

4. A flame retardant resin composition as claimed in claim 3, wherein the resin content of said ethylene/lower alkyl methacrylate copolymer is from 50 to 90 wt%; and the lower alkyl methacrylate content of said ethylene/lower alkyl methacrylate copolymer is from 10 to 50 wt%.

5. A flame retardant resin composition as claimed in claim 1, wherein said lower alkyl methacrylate is methyl methacrylate, ethyl methacrylate or propyl methacrylate.

6. A flame retardant resin composition as claimed in claim 5, wherein said lower alkyl methacrylate is methyl methacrylate.

7. A flame retardant resin composition as claimed in claim 1, wherein said organic flame retarder is tetrabromobutane, perchloropentacyclodecane, tetrabromobisphenol A, chlorinated paraffin, bromotriphenylphosphate, decabromobiphenyl, decabromodiphenyl oxide, and bromoepoxide.

8. A flame retardant resin composition as claimed in claim 7, wherein said organic flame retarder is decabromobiphenyl or decabromodiphenyl oxide.

9. A flame retardant resin composition as claimed in claim 1, wherein said inorganic flame retarder is an oxide of antimony, arsenic or tin; or a sulfide of antimony, arsenic or tin.

10. A flame retardant resin composition as claimed in claim 9, wherein said inorganic flame retarder is antimony trioxide.

11. A flame retardant resin composition as claimed in claim 1, wherein said inorganic filler is asbestos, talc, clay, mica, zinc borate, aluminum hydroxide, calcium carbonate, barium sulfate or magnesium oxide.

12. A flame retardant resin composition as claimed in claim 1, wherein said inorganic filler is talc, clay, zinc borate.

13. A flame retardant resin composition as claimed in claim 1, wherein the amount of said organic flame retarder is from 10 to 50 parts by weight; the amount of said inorganic flame retarder is from 1 to 30 parts by weight; and the amount of said inorganic filler is from 5 to 50 parts by weight, all based on 100 parts by weight of said graftmer.

14. A flame retardant resin composition as claimed in claim 13, wherein the amount of said organic flame retarder is from 15 to 40 parts by weight; the amount of said inorganic flame retarder is from 5 to 25 parts by weight; and the amount of said inorganic filler is from 5 to 25 parts by weight, all based on 100 parts by weight of said graftmer.

15. A flame retardant insulated cable comprising:

(a) a conductor;

(b) an insulator comprising polyethylene having a high softening point covering said conductor; and

(c) a flame retardant resin composition comprising a resin material containing as a main component

(A) a graft copolymer prepared by graft copolymerizing an ethylene/lower alkyl methacrylate copolymer with vinyl chloride; and

(B) at least one member selected from the group consisting of

(i) an organic flame retarder,

(ii) an inorganic flame retarder, and

(iii) an inorganic filler.

16. A flame retardant insulated cable as claimed in claim 15, wherein said flame retardant resin composition further comprising (C) a hindered amine light stabilizer.